Symposium: 25 Years of ISIS Muons

Muonium in Semiconductors as a Model for Hydrogen Impurities

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We have been involved in examining Mu as an experimentally accessible analogue for isolated hydrogen impurities in semiconductors for essentially the full time that the ISIS MuSR Facility has been operational. Following a brief discussion of major contributions of the MuSR results to this field over the years, a few case studies will be presented to demonstrate the methods applied to this problem and the detailed knowledge regarding the physical and electronic structures of H/Mu which can be obtained. Dynamics associated with the observed Mu defect centers will be discussed, including both local motion and long range diffusion, as well as numerous transitions among the defect sites and charge-states. We will focus on results that provided experimental verification that the charge-state transition levels for hydrogen are pinned at a constant absolute energy and established the (negative) value for the electrostatic repulsion energy *U* for the Mu 'isotope' of H in several of these semiconducting materials. Recent evidence that the acceptor level for Mu at the T-site in Ge lies in the valence band and the consequences for hydrogen in Ge will be presented. Data that we are currently using in an attempt to measure how deep in the valence band the energy level for the Mu^- core of a shallow Mu acceptor state lies will be briefly discussed as well.

25 Years of ISIS Muons

Muonium in Semiconductors as a Model for Hydrogen Impurities

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Outline

Brief introduction to Hydrogen in Semiconductors

Major contributions from MuSR

Muonium in Si, III-Vs (Cubic) and III-Nitrides (Hexagonal)

- Physical and electronic structures
- Motion of Mu: dependence on charge-state
- Dynamics of Mu site changes & charge-state transitions

H / Mu as an electrically active impurity / dopant

- Negative – U impurities and defect level pinning
- Shallow Mu donors
- Shallow Mu acceptors: VB-resonant Mu^- in Ge & SiGe alloys

Conclusions

H in Semiconductors

Isolated hydrogen – H^+, H^0, H^-

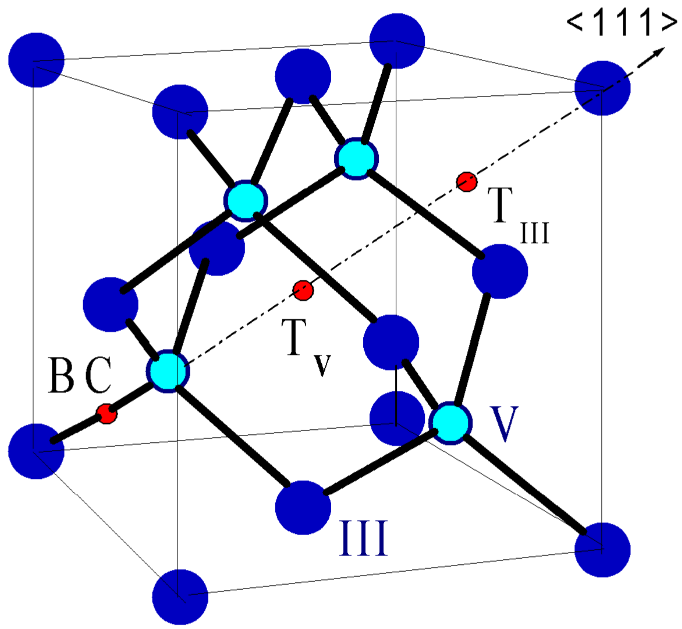
H is highly mobile and
reacts with other defects

Most experiments probe
H - Defect complexes

H 'passivates' active defects

Isolated H seen only after
low-T proton implantation

Much studied defect by
computational methods



Expected sites for H/Mu

In elemental - diamond str

BC is H^0 low energy site

H^+ is stable at BC

H^- is stable at T-site

T-site metastable for H^0

Effects from Hydrogen in Semiconductors

Hydrogen normally acts as a deep compensating defect
Meaning H acts against the prevailing conductivity type
H acts as Acceptor (H^-) in n-type; Donor (H^+) in p-type

Due to high mobility and strong reactivity H passivates many electrically and / or optically active impurities as a result of the H defect chemistry within the material

Hydrogen also activates some iso-electronic impurities
Example: a Si-H pair in Ge becomes a shallow acceptor

Mu is a light 'isotope' of H $M_{Mu} \sim M_H / 9$

H and Mu electronic states are nearly identical since the reduced electronic masses differ only slightly

Significant Contributions from MuSR

- Muonium results provide much of the experimental evidence for comparison with theory for Hydrogen

First Major Contribution

- 1987 Mu* identified as BC^0 center; H^0 ground state

  Mu* hyperfine spectrum scales w/ AA-9 EPR signal in Si

  Gorelkinski & Nevinnyi, *Zh Tekh Fiz* 13 (1987) 105

  Nuclear HF splittings demonstrate BC structure (GaAs)

Symons, *Hyp Int* 19 (1984) 771; Cox and Symons, *Chem Phys Lett 126* (1986) 516

Estle etal, *Hyp Int* 32 (1986) 637; Estreicher, *Phys Rev B* 36 (1987) 9122

Kiefl etal, *Phys Rev Lett* 58 (1987) 1780; Kiefl etal, *Phys Rev Lett* 60 (1988) 224

- 1992-94 Metastable Mu_T^0 center was linked with the highly mobile "transition state" for H^0 diffusion

  Lichti etal, *Mater Sci Forum* 83-87 (1992) 1115

- 1994-97 Remind *Defects in Semiconductors* community that equilibrium is dynamic - fast Mu charge/site cycles

  Estle etal, *Mater Sci Forum* 258-263 (1997) 849

- 1999 Clear evidence of negatively-charged ionic state

  Hitti etal, *Phys Rev B* 59 (1999) 4918

- 1999-2001 Mu shallow donors – Hydrogen as a dopant

  Gil etal, *Phys Rev Lett* 83 (1999) 5294; Cox etal, *Phys Rev Lett* 86 (2001) 2601

- 2008 Mu Confirms theory that H defect levels pinned

  Van der Walle & Neugebauer, *Nature 423* (2003) 626

  Lichti Chow & Cox, *Phys Rev Lett* 101 (2008) 136403

- 2009 Confirm H / Mu as a donor in TCO electrodes

  King etal *Phys Rev B* 80 (2009) 081201R

Properties of Muonium Centers

Physical and electronic structure of Mu centers

Spin precession spectra (TF-μSR) show two Mu^0 centers
HF level crossing (ALCR) refines Mu^0 physical structures
Quadrupolar-LCR yields Mu^+ and Mu^- physical structures

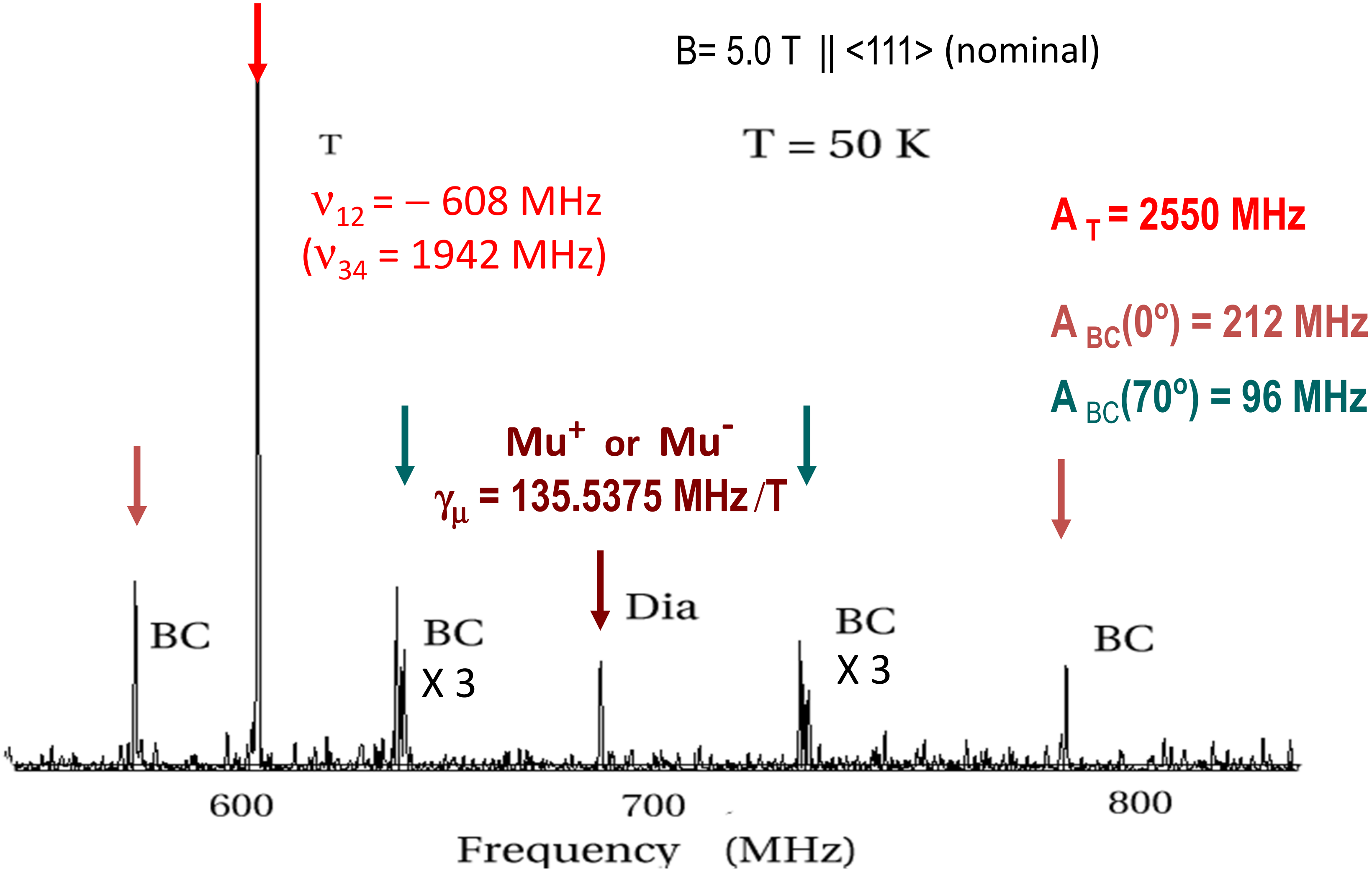
Local motion and diffusion of Mu centers

Relaxation rates in longitudinal fields (LF) $\lambda(T,B)$ for Mu^0
Depolarization in zero applied field (ZF) for Mu^+, Mu^-

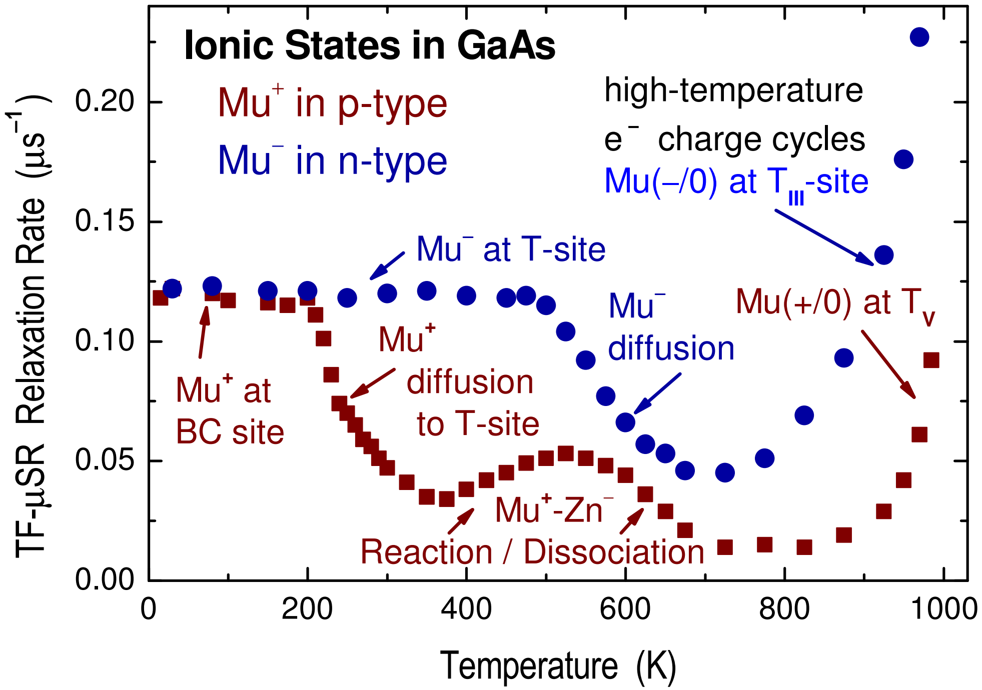
Dynamics of site-change and charge-state transitions

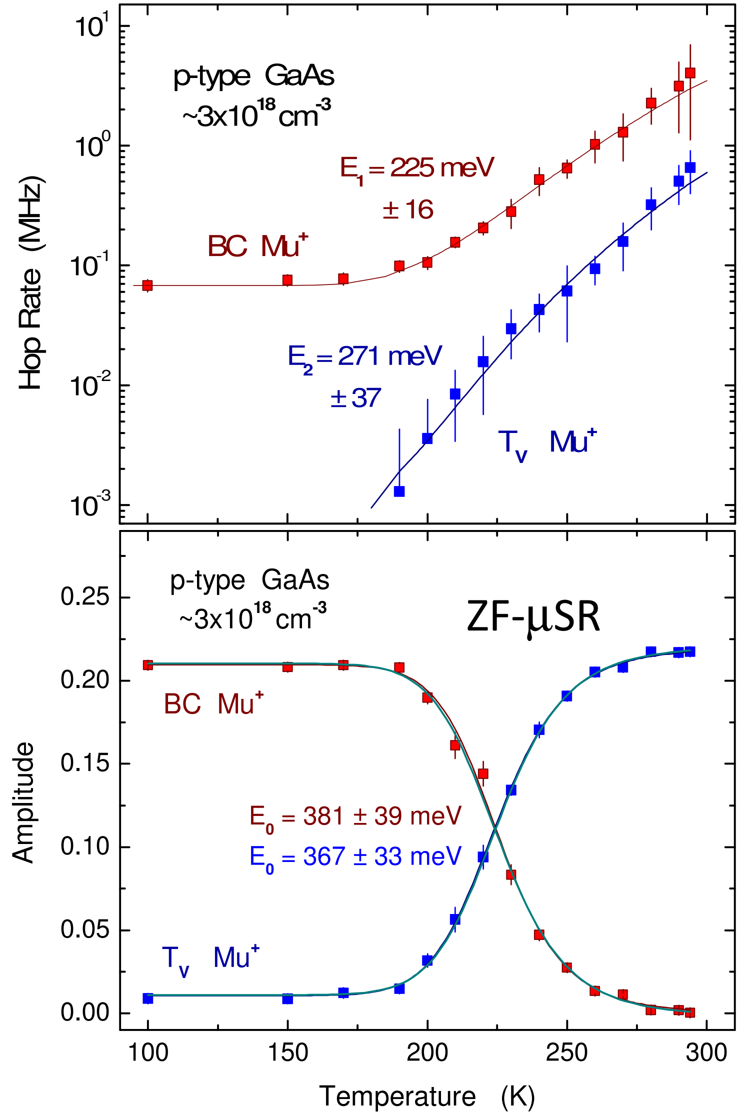
T-dependent line widths in TF-μSR (lifetime broadening)
T-dependent amplitudes in multi-signal fits
RF-μSR (longitudinal fields) detects slowly formed states
LF relaxation rates - sensitive to cyclic processes

Hyperfine Spectroscopy: Mu^0 Centers in GaP



Separation of Mu^+ and Mu^- Signals





Mu^+ and Mu^- have same TF-μSR frequency

But have very different motional properties

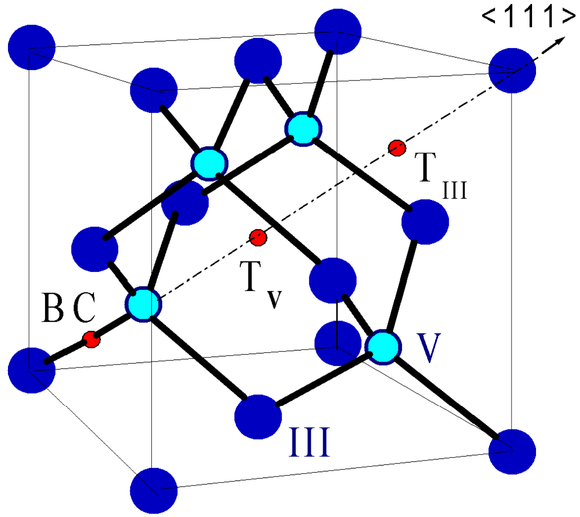
Easy to distinguish from 200K to 500K

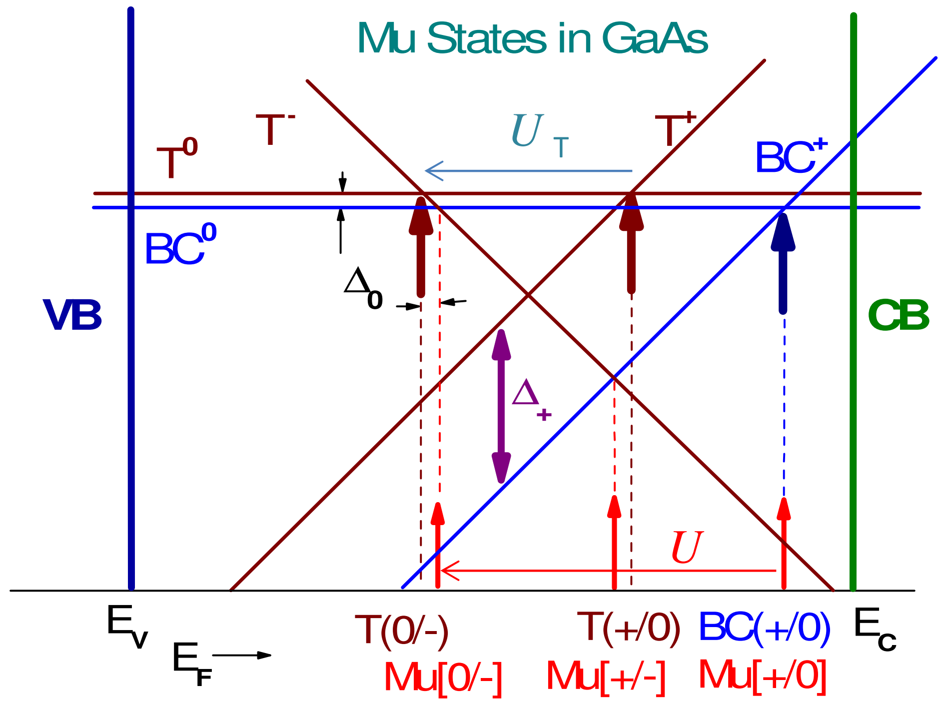
Mu^+ diffusion changes character near 225K

BC-BC hops <225K to T_V-T_V motion >225K

Lichti etal, PRB 76 (2007) 045221

Energy Relationships for Mu in GaAs





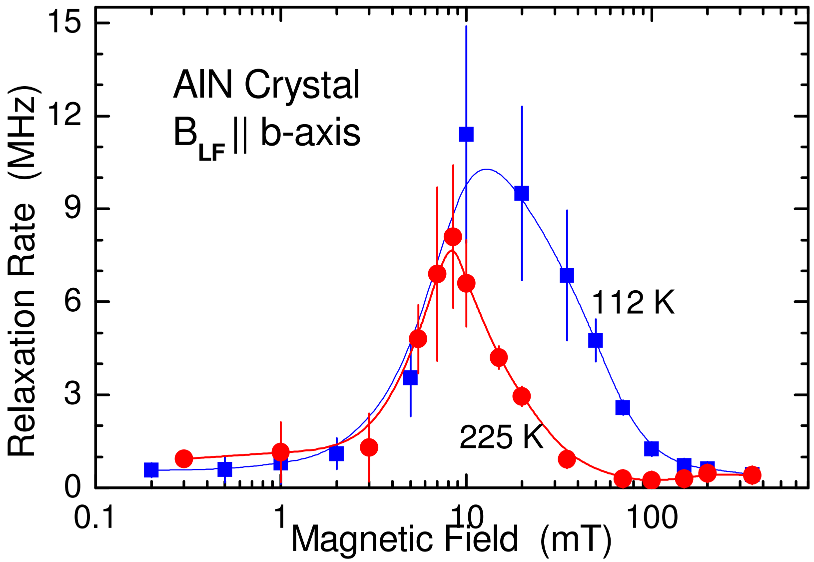
Sites for Mu (or H) in GaAs

Mu^0 BC lowest, $E(T) = E(BC) + \Delta_0$
Mu^+ BC lowest, $E(T_{AS}) = E(BC) + \Delta_+$
Mu^- T_{Ga} is only stable location
Site change: $T^0 \rightarrow BC^0$ $E_a = 0.4$ eV ?
$BC^+ \rightarrow T^+$ $E_a = 0.37$ eV
T-site ions stabilized by 0.22 eV

Formation Energy Diagram

$\Delta_0 = 0.045$ eV $\Delta_+ = 0.32$ eV
$E_A(T_{Ga}) - E_V = 0.55$ eV
$E_C - E_D(BC) = 0.17$eV; $E_C - E_D(T_{As}) = 0.45$ eV
$U = -0.57$ eV $U_T = -0.36$ eV
Lichti etal PRB 76 (2007) 045221

Motion of Mu^0 centers in AlN

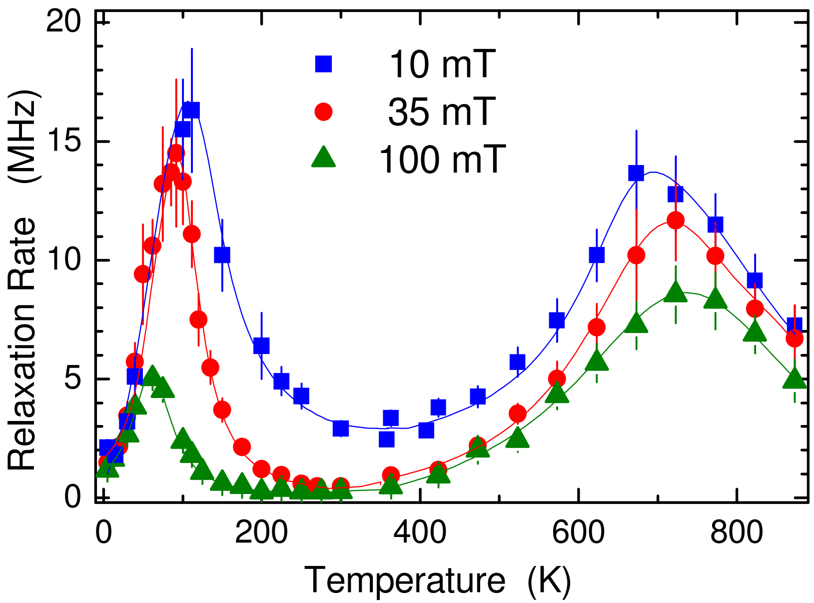


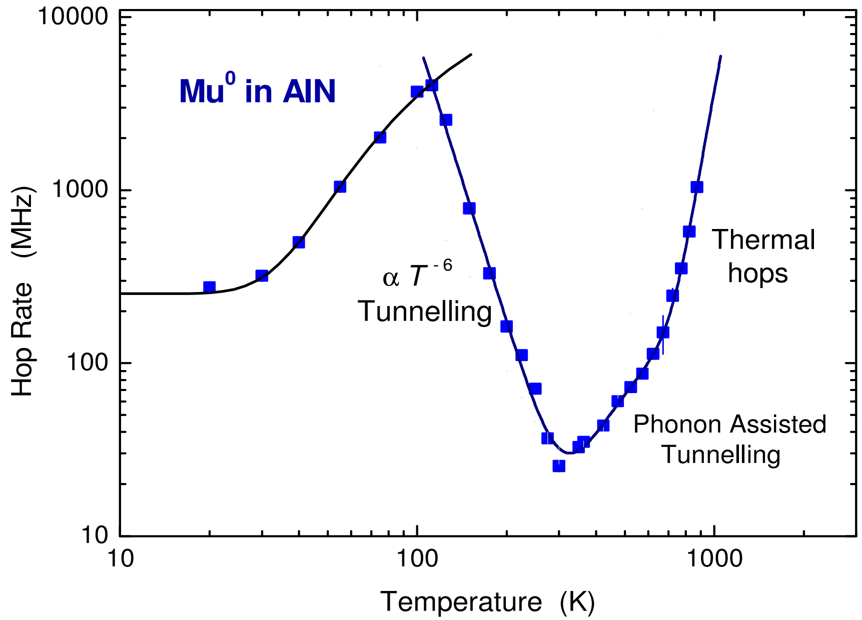
Hop rates (τ_c^{-1}) obtained from longitudinal relaxation rates as

$$T_1^{-1}(B) = M^2(B) \cdot \frac{\tau_c}{1 + w_{12}^2(B)\tau_c} + C$$

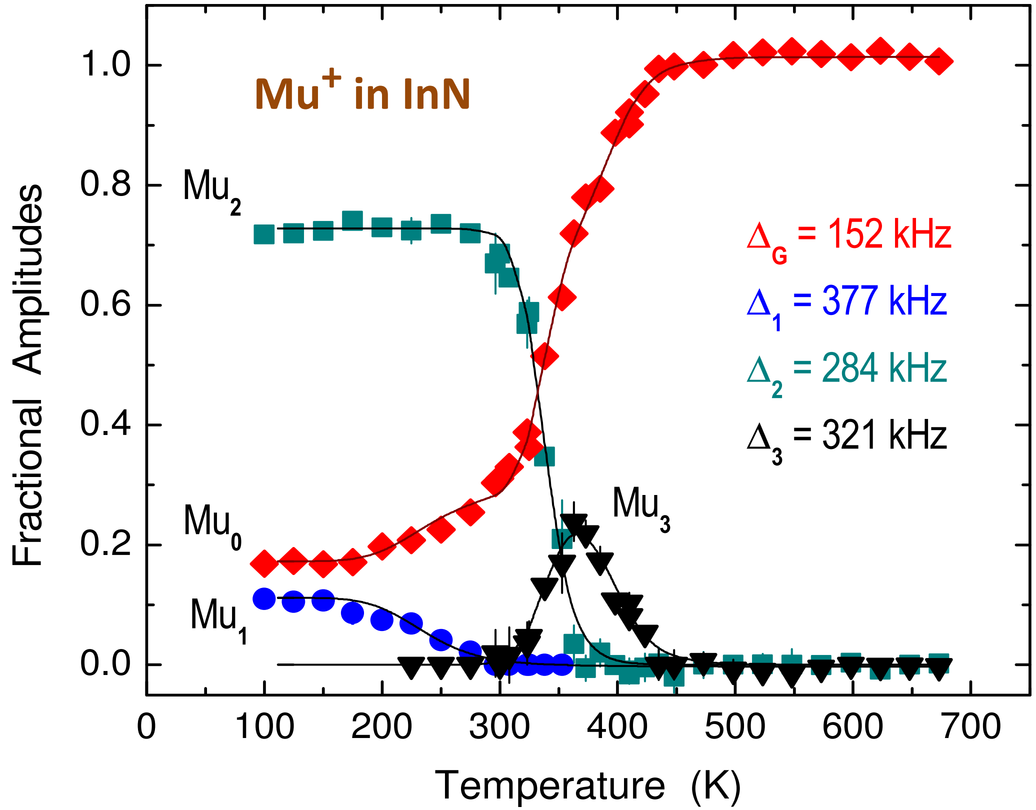
Can use T_1^{-1} as function of BLF to extract ν_{hop} and C at each T

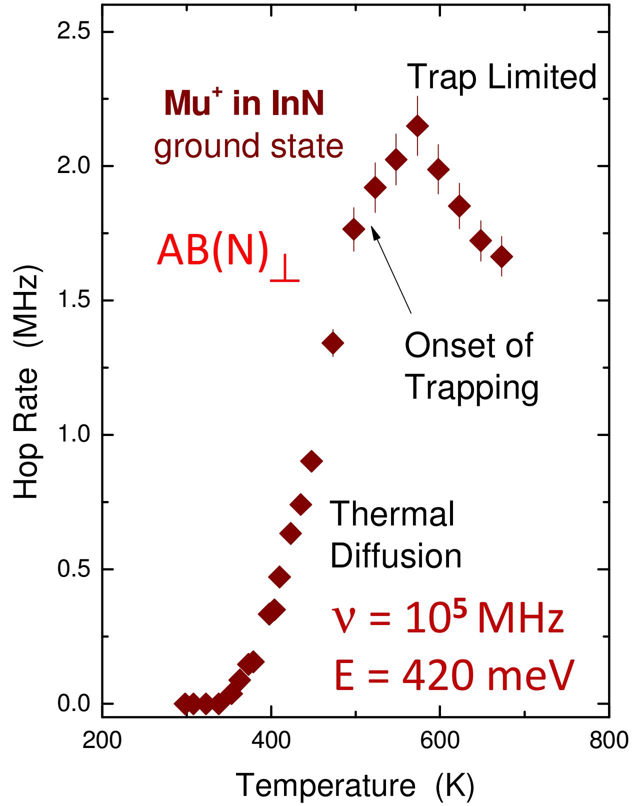
Bani-Salameh etal *PRB* 74(2006)245203





Mu^+ Sites and Diffusive Motion in InN





Theory predicts four local minima for different orientations of a N-H bond

We observed four different Kubo-Toyabe signals (3 static, 1 dynamic) in ZF data

Mu_0 shows local tunneling (80 kHz , T <320K) ; thermal diffusion for T >320K

Obtained diffusion barrier and characteristic energies for trapping and release

Celebi etal, Phys Rev B 74(2006)245219

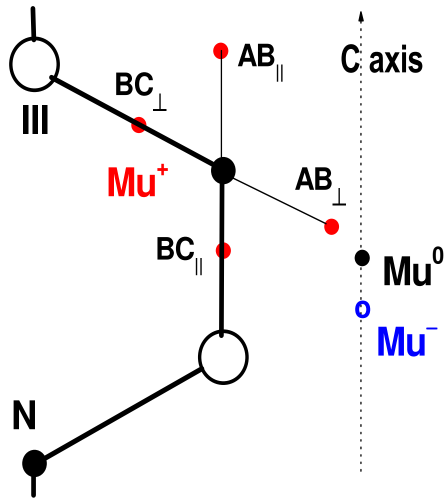
Summary re Properties of Mu Centers

Cubic Semiconductors

- Identify Mu^0 by HF spectra and ionic centers by motion
- Mu_T^0 is very mobile at all temperatures compared to all others
- Very different motion characteristics for different charge states
- High-*T* diffusion often controlled by trap and release processes
- Determined site and charge-state transition dynamics (Si, GaAs)
- Observe numerous rapid cyclic transition sequences
- Observed interactions with dopants (Mu passivation reactions)

Hexagonal (Wurtzite) Materials

- Mu sites in III-nitrides obtained
- Charge-state motional properties
- Probed local motion vs diffusion



Hydrogen as a Dopant: Shallow Mu Donors

Most early examples of Shallow Mu Donor states

(CdS, CdSe, CdTe, ZnO)

Gil etal, *PRL* 83 (1999) 5294

Gil etal, *PRB* 64 (2001) 075205

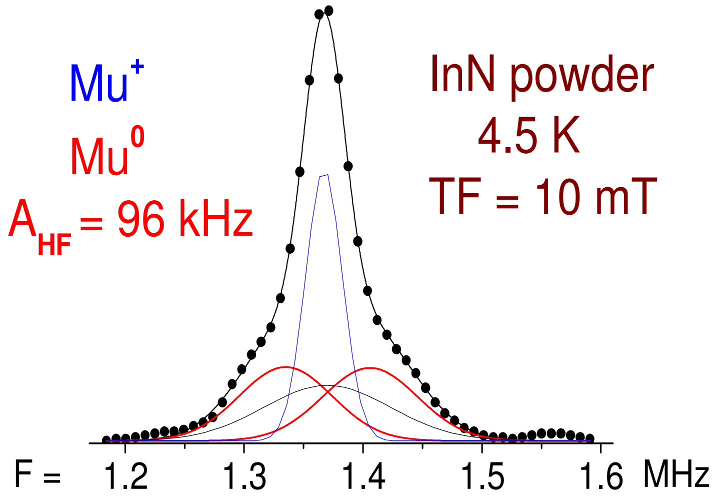
Cox etal, *PRL* 86 (2001) 2601

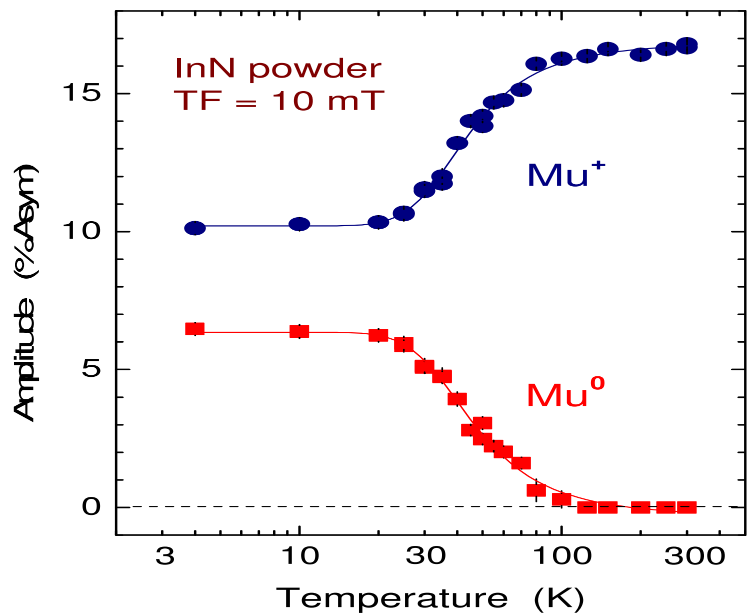
had well resolved hyperfine lines observed as separate satellites and were a large fraction of the total signal - obvious beats

InN is more typical – with smaller hyperfine constants and poorly resolved satellite (hf) lines

Davis etal, *APL* 82 (2003) 592

Other materials show smaller Mu^0 amplitudes, beats are not as clear



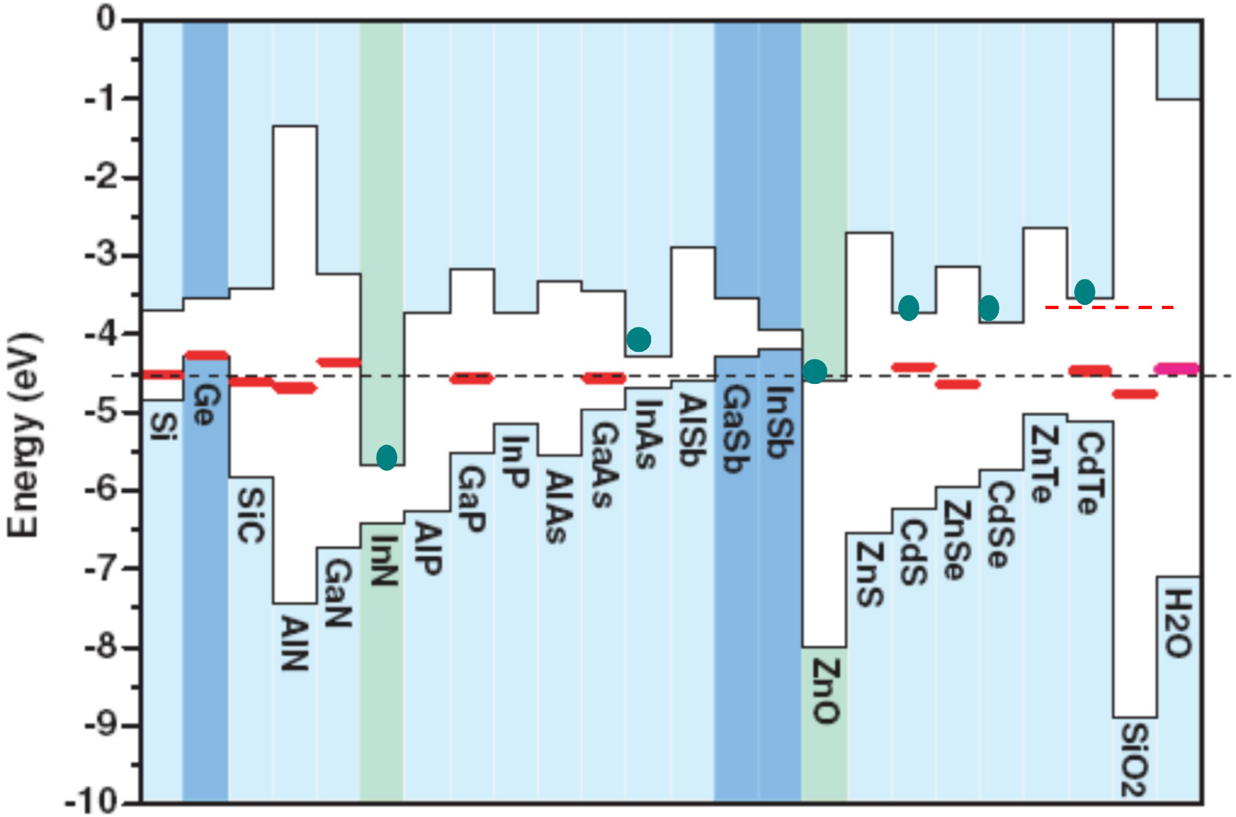


Prediction of H Defect-Level Pinning

Thermodynamic level for change in hydrogen charge-state H^+ to H^- with E_F H(+/-) was predicted to be at a 'universal' energy
(due to negative *U*)

If H(+/-) in CB or VB H will dope material n-type or p-type

We set out to test these predictions using Muonium



● Shallow Mu^0 signal reported (CdTe upper limit)

Van de Walle and Neugebauer
Nature 423 (2003) 626

Relevant Experimental Measurements

Ionization Transitions

$Mu_{BC}^{0} \longrightarrow Mu_{BC}^{+} + e^{-}$

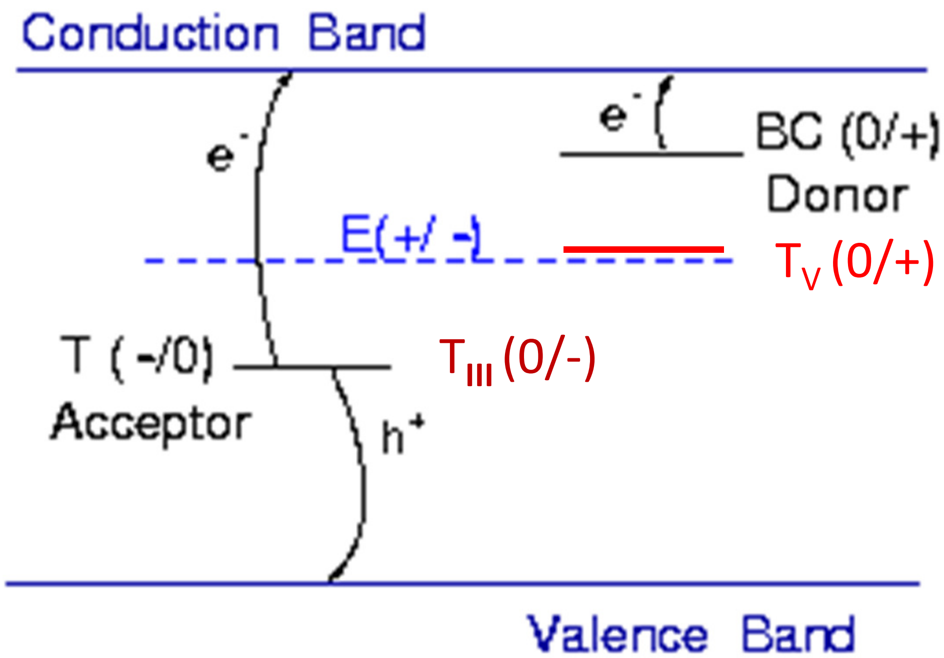
Gives Mu(0/+) if
BC is lowest Mu^0 site

$Mu_{T}^{0} \longrightarrow Mu_{T}^{-} + h^{+}$

$Mu_{T}^{-} \longrightarrow Mu_{T}^{0} + e^{-}$

Either would give
Mu(–/0) if T_{III} site
lies lowest for Mu^0

Lichti etal PRB 76 (2007) 045221



GaAs data:

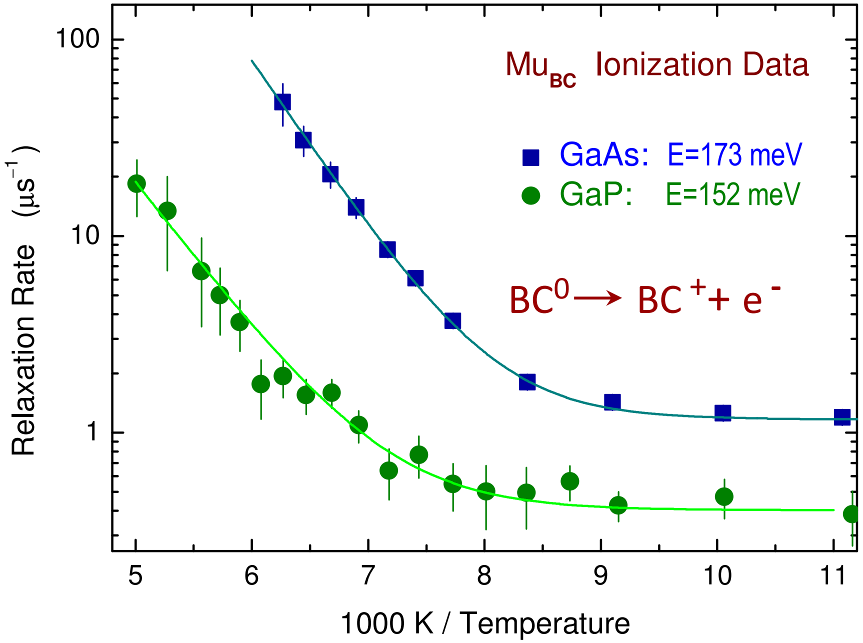
$BC(0/+) = E_c - 0.17$ eV

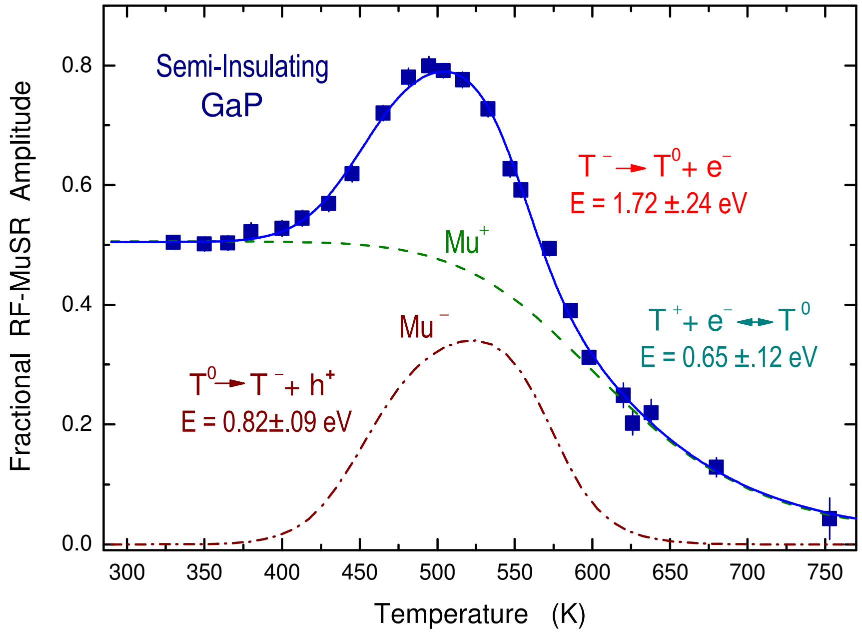
$T_V(0/+) = E_c - 0.45$ eV

$T_{III}(0/-) = E_V + 0.55$ eV

$T_{III}(-/0) = E_c - 1.02$ eV

MuSR Data on Donor and Acceptor Levels





Mu Donor Level in GaAs

E_C – 0.173(4) eV

(average of six samples)

Lichti etal PRB 76 (2008) 045221

Mu Donor Level in GaP

E_C – 0.152(18) eV

(from single sample)

Vernon etal Physica B 404 (2009) 820

Results from RF-MuSR resonance

T-site Mu Acceptor Levels at

E_V + 0.56(3) eV for GaAs

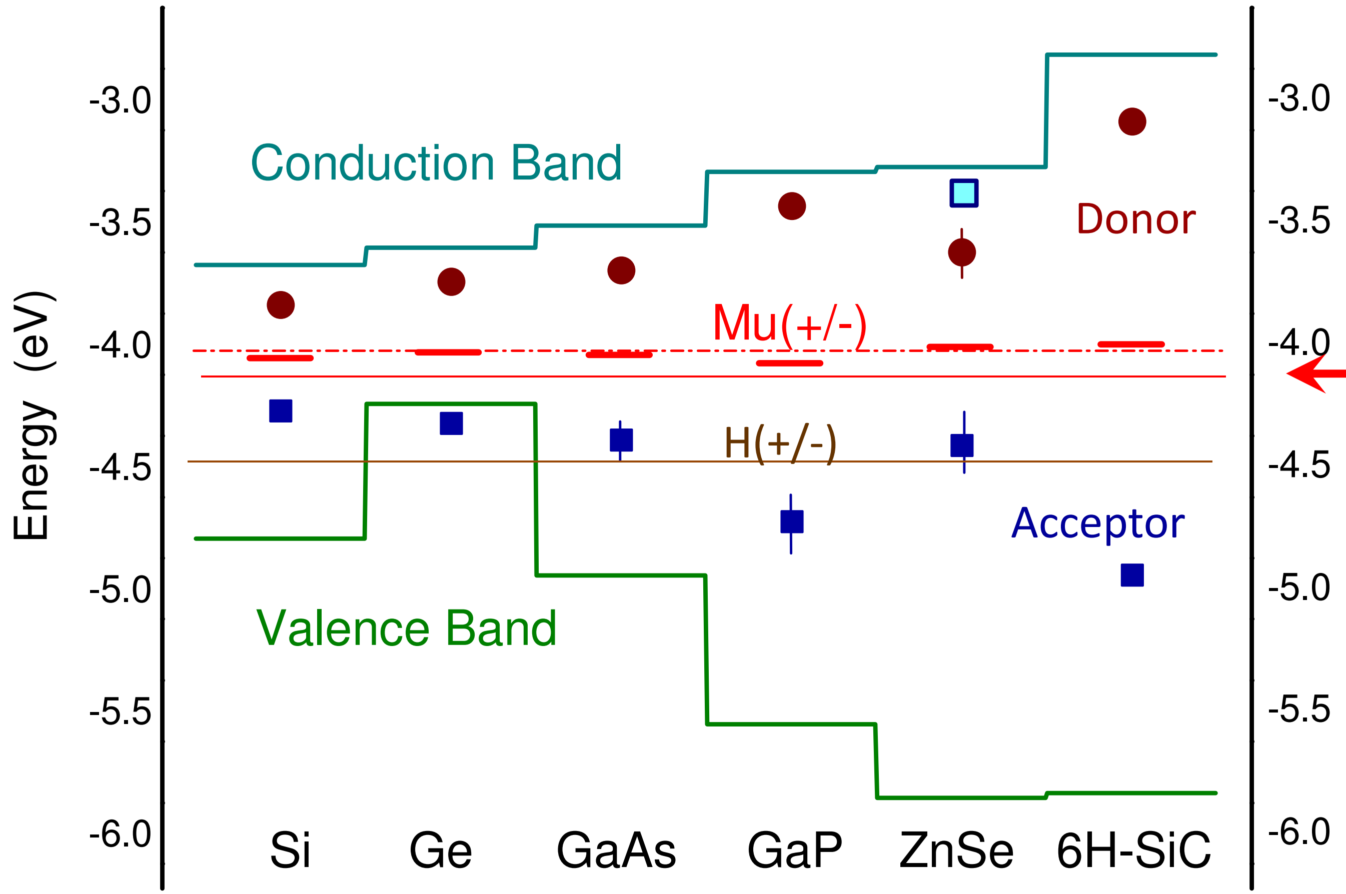
E_C – 1.05(8) eV

E_V + 0.82(9) eV for GaP $T_{0/-}$

E_C – 1.72(24) eV from $T_{-/0}$

yields coulomb energy of 0.32 eV

Muonium Results: Mu Defect Levels



H(+/-) estimate based on Mu results

Lower by 30-70 meV (ZPEs)

Alignments and H predictions from Van de Walle and Neugebauer

Lichti, Chow & Cox *PRL* 101 (2008) 136403

Mu Defect Levels in $Si_{1-x}Ge_x$ Alloys

Compare H *vs* Mu in Si and Ge
$-U$ larger for H than Mu

Strongest evidence thus far for
shallow Mu acceptor states

Two T-site Mu^0 's in alloys
different hyperfine constants

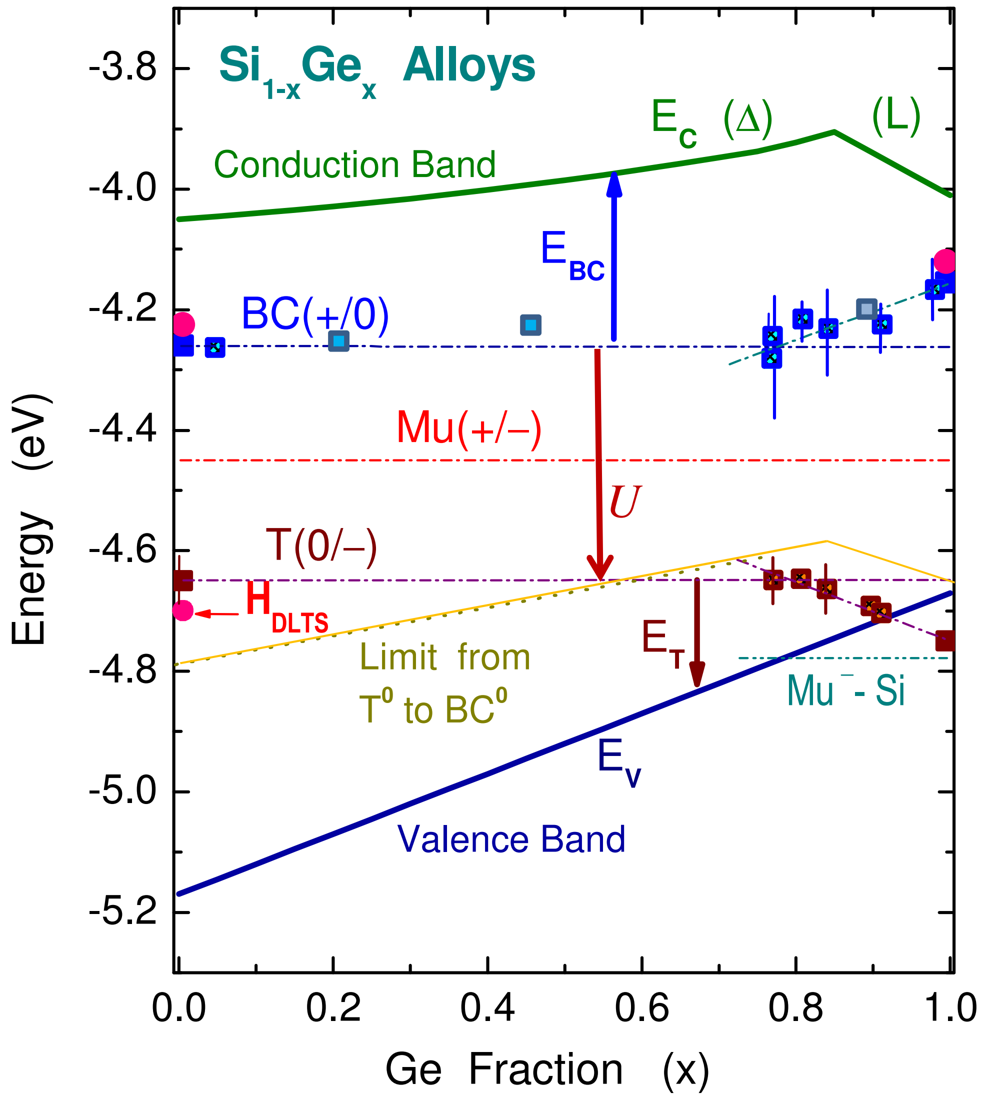
Localized acceptor level enters
valence band near x = 0.92

Evidence for two shallow Mu
acceptor states

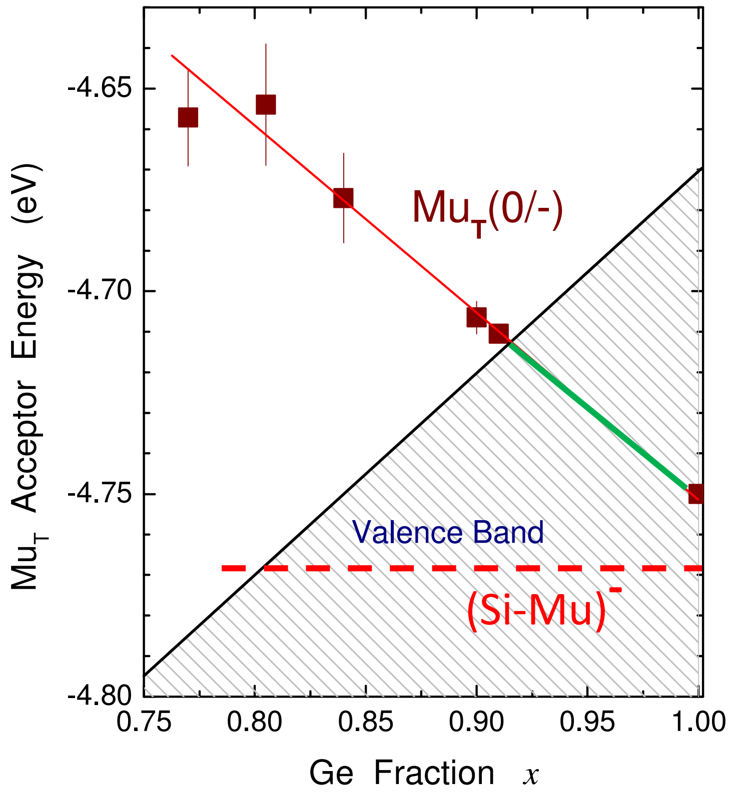
one in Ge-like region

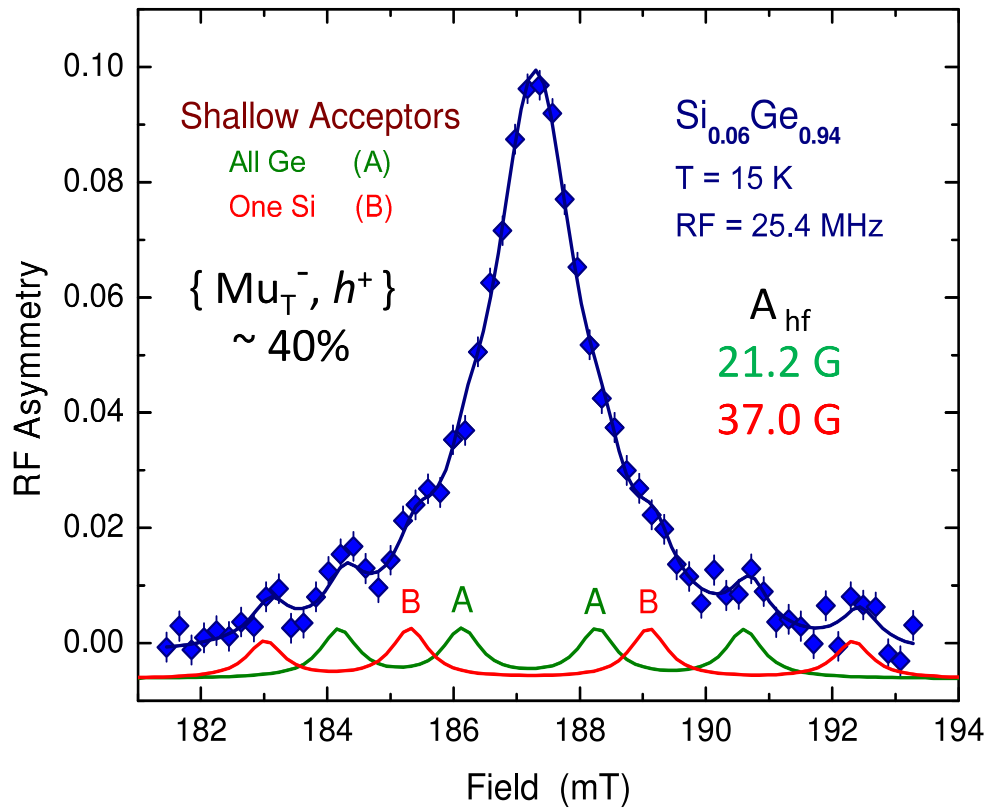
second as Mu^- - Si pair

Carroll etal, PRB 82 (2010) 205205



Spectroscopic Evidence of Shallow Mu Acceptor





When localized acceptor energy falls in Valence Band (x > 0.92)
Expect a shallow Mu acceptor

Top of valence band has J = 3/2, thus shallow acceptor will have 4-line spectra
Two SA: one isotropic, other lower sym

Hints of Shallow Acceptor in TF-μSR Spectra

Small beats were also observed in spin precession spectra for the $x = 0.84$ and $x = 0.81$ samples

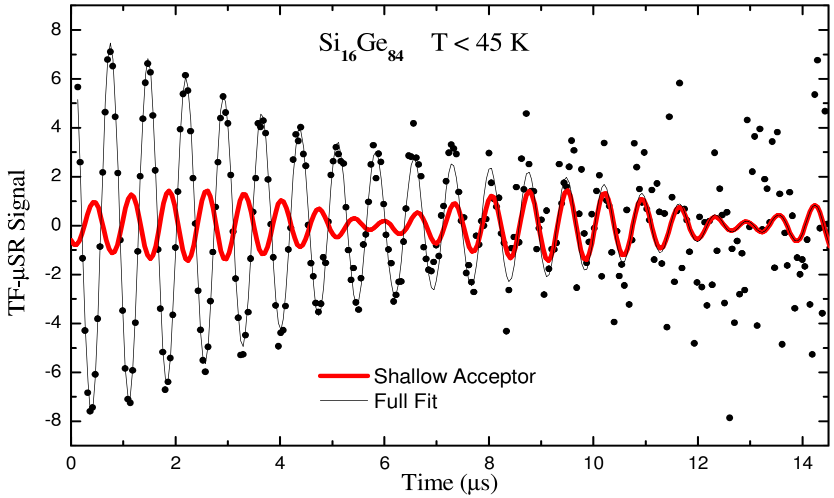
Phases were different at 10 μs compared to initial phases

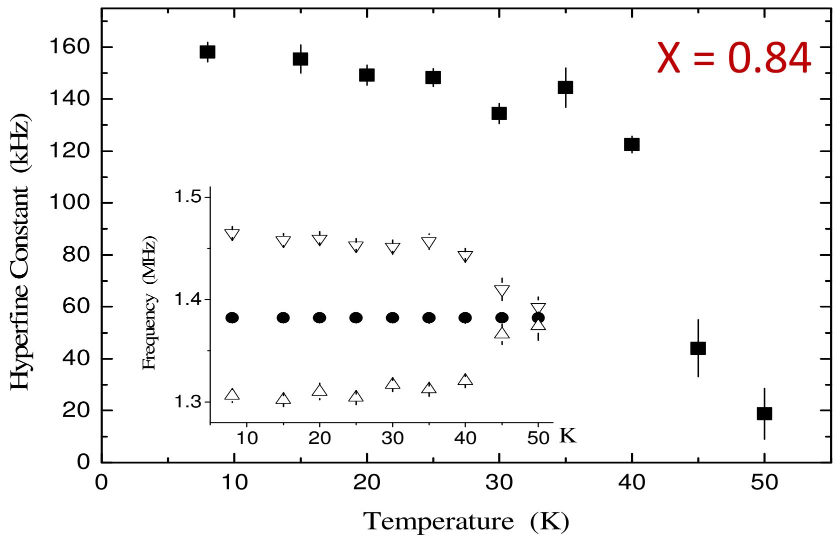
When fit as 2-line HF spectra
$A_{0.84} = 160$ kHz $A_{0.81} \sim 120$ kHz

Would also fit with a lot larger splitting but with a field offset

Suggests the low-symmetry SA Is still present with up to 19% Si And A decreases as x decreases

Work to do on these spectra





Conclusions re Electrical Activity of H/Mu

- Mu Donor (BC site) and Acceptor (T site) ionization energies locate the Mu(+/-) level in six semiconductors; yield (-)U
- Results are consistent with a constant Mu(+/-) energy
- Mu(+/-) above predicted H(+/-): after adjusting for ZPE Mu results imply H(+/-) is ~ 0.4 eV higher than predicted
- Fewer materials doped p-type by H (GaSb, InSb, Ge ?)
- More materials doped n-type by H (InAs, CdS, CdSe ?)
- Shallow Mu donors observed in many TCO materials
- Shallow Mu acceptors observed in Ge-rich SiGe alloys

  Recent data on H in Ge suggests only a negative charge state, H^{-}
- MuSR requires only Mu(0/+) in CB or Mu(-/0) in VB to see shallow states. This makes Mu shallow state observation suggestive but not conclusive re doping by hydrogen